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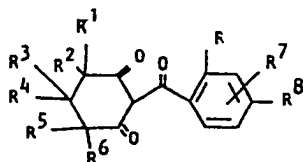
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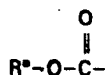
64 Certain-2-(2'-alkylbenzoyl)-1,3-cyclohexanediones.

57 Compounds of the formula



wherein R is C<sub>1</sub>-C<sub>4</sub> alkyl or CF<sub>3</sub>; R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;  
R<sup>2</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl or

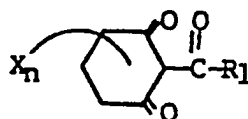
or C<sub>1</sub>-C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined with the proviso that R<sup>7</sup> is not attached to the 6-position are effective as herbicides.



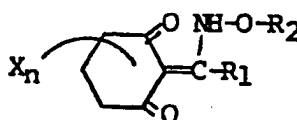
wherein R<sup>a</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>1</sup> and R<sup>2</sup> together are alkylene having 3 to 6 carbon atoms; R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>4</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>6</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; and R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>, wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>c</sup>C(O)- wherein R<sup>c</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl

CERTAIN 2-(2'-ALKYLBENZOYL)-1,3-CYCLOHEXANEDIONESBackground of the Invention

Compounds having the structural formula



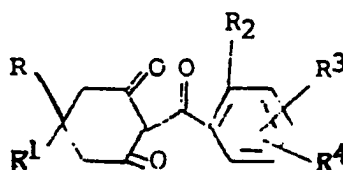
wherein X can be an alkyl, n can be 0, 1, or 2, and R<sub>1</sub> can be phenyl or substituted phenyl are described in Japanese Patent Application 84632-1974 as being intermediates for the preparation of herbicidal compounds of the formula



wherein R<sub>1</sub>, X, and n are as defined above and R<sub>2</sub> is alkyl, alkenyl, or alkynyl. Specifically taught herbicidal compounds of this latter group are those where n is 2, X is 5,5-dimethyl, R<sub>2</sub> is allyl and R<sub>1</sub> is phenyl, 4-chlorophenyl or 4-methoxyphenyl.

The precursor intermediates for these three specifically taught compounds have no or almost no herbicidal activity.

European Patent Application No. 83 102 599.4 was published October 5, 1983 and relates to certain novel 2-(2-substituted benzoyl)-cyclohexane-1,3-diones as herbicides. The compounds have the following structural formula



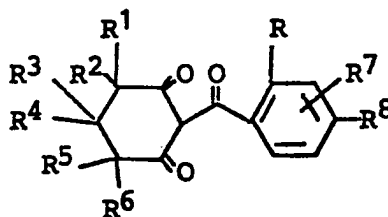
wherein R and R<sup>1</sup> are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>2</sup> is chlorine, bromine, or iodine; R<sup>3</sup> is hydrogen or halogen; and R<sup>4</sup> is hydrogen, chlorine, bromine, iodine, C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> alkoxy, nitro or trifluoromethyl.

### Description of the Invention

This invention relates to 2-(2-alkylbenzoyl)-1,3-cyclohexane-  
5 diones and their use as herbicides.

One embodiment of this invention is an herbicidal composition comprising an herbicidally active 2-benzoyl-1,3-cyclohexanedione and an inert carrier therefor wherein the 2-position of the benzoyl moiety is substituted with C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, optionally substituted with halogen, more preferably methyl or CF<sub>3</sub> and the 4-position preferably is substituted with an electron withdrawing group, such as halogen, cyano, CF<sub>3</sub> or nitro. The 4-, 5- and 6-positions of the 1,3-cyclohexanedione moiety can be substituted, preferably with the groups herein-  
after recited. More preferably, the 1,3-cyclohexanedione moiety has no  
substitution or the 4- or 6-positions are substituted with one or two  
methyl groups. The 3-, 4- and 5-positions of the benzoyl moiety can be substituted, preferably with the groups hereinafter recited.

Also embodied within the scope of this invention are novel compounds having the following structural formula



wherein

R is C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, optionally substituted with halogen, more preferably methyl and CF<sub>3</sub>;

R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably R<sup>1</sup> is hydrogen or methyl;

R<sup>2</sup> is hydrogen; C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl or



wherein Ra is C<sub>1</sub>-C<sub>4</sub> alkyl, most preferably R<sup>2</sup> is hydrogen or methyl; or

$R^1$  and  $R^2$  together are alkylene having 3 to 6 carbon atoms;

$R^3$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl; most preferably  $R^3$  is hydrogen or methyl;

$R^4$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl; most preferably  $R^4$  is hydrogen or methyl;

$R^5$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl; most preferably  $R^5$  is hydrogen or methyl;

$R^6$  is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably C<sub>1</sub>-C<sub>2</sub> alkyl, more preferably methyl, most preferably  $R^6$  is hydrogen;

$R^7$  and  $R^8$  independently are (1) hydrogen; (2) halogen, preferably chlorine, fluorine or bromine; (3) C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy, preferably methoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl, more preferably trifluoromethyl; (9)  $R^bSO_n$ - wherein n is the integer 0, 1 or 2, preferably 2; and

$R^b$  is (a) C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl;

(b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano, preferably chloromethyl, trifluoromethyl or cyanomethyl;

(c) phenyl; or

(d) benzyl;

(10)  $-NR^cR^d$  wherein

$R^c$  and  $R^d$  independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

(11)  $R^eC(O)-$  wherein

$R^e$  is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; or

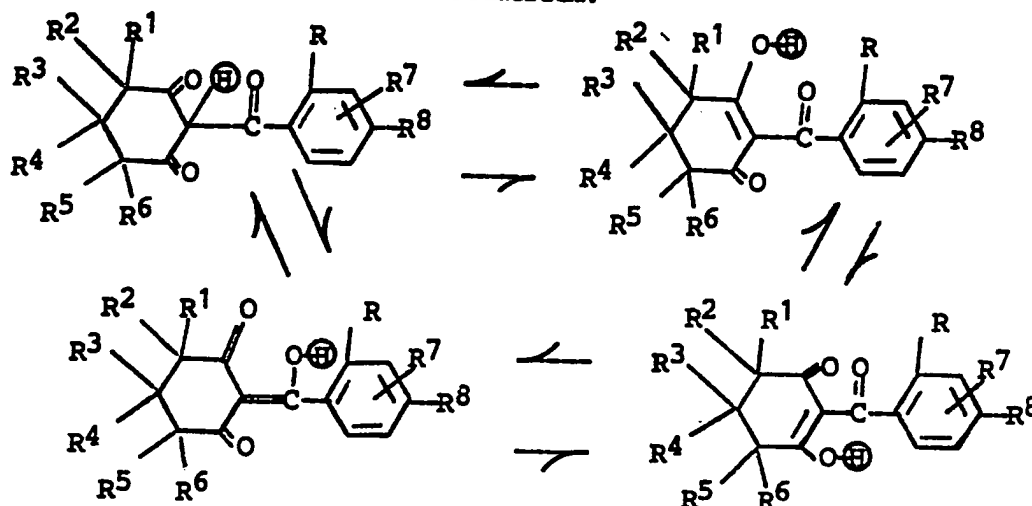
(12)  $-SO_2NR^cR^d$  wherein  $R^c$  and  $R^d$  are as defined, with the proviso that  $R^7$  is not attached to the 6-position.

The term "C<sub>1</sub>-C<sub>4</sub> alkyl" includes methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl and t-butyl. The term "halogen" includes chlorine, bromine, iodine and fluorine. The term "C<sub>1</sub>-C<sub>4</sub> alkoxy" includes methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, isobutoxy and t-butoxy. The term "haloalkyl" includes the eight alkyl groups with one or more hydrogens replaced by chloro, bromo, iodo or fluoro.

Preferably,  $R^7$  is in the 3-position. Most preferably  $R^7$  is hydrogen and  $R^8$  is hydrogen, chlorine, bromine, fluorine, CF<sub>3</sub>, or  $R^bSO_2$  wherein  $R^b$  is C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl.

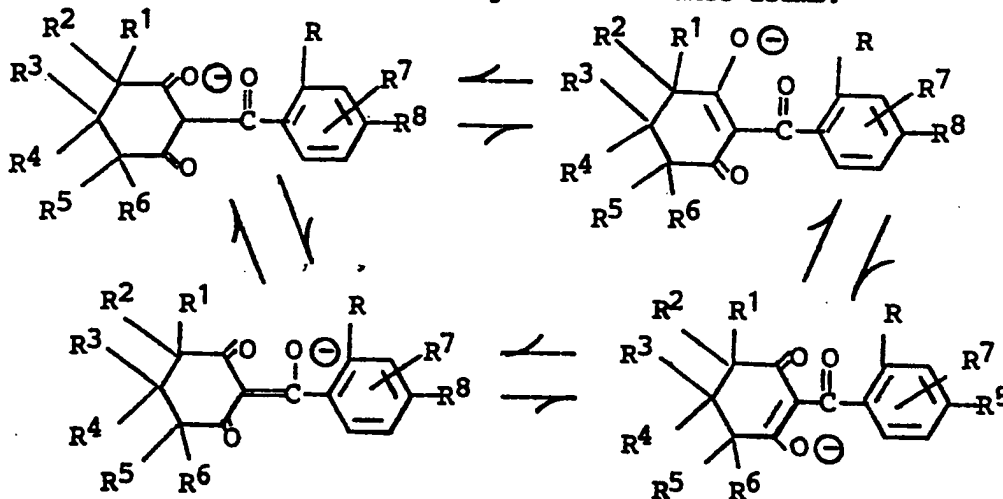
Salts of the above-described compounds (as defined hereinafter) are also the subject of the instant invention.

The compounds of this invention can have the following four structural formulae because of tautomerism:



5 wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are as defined above.

The circled proton on each of the four tautomers is reasonably labile. These protons are acidic and can be removed by any base to give a salt having an anion of the following four resonance forms:



wherein R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are as defined above.

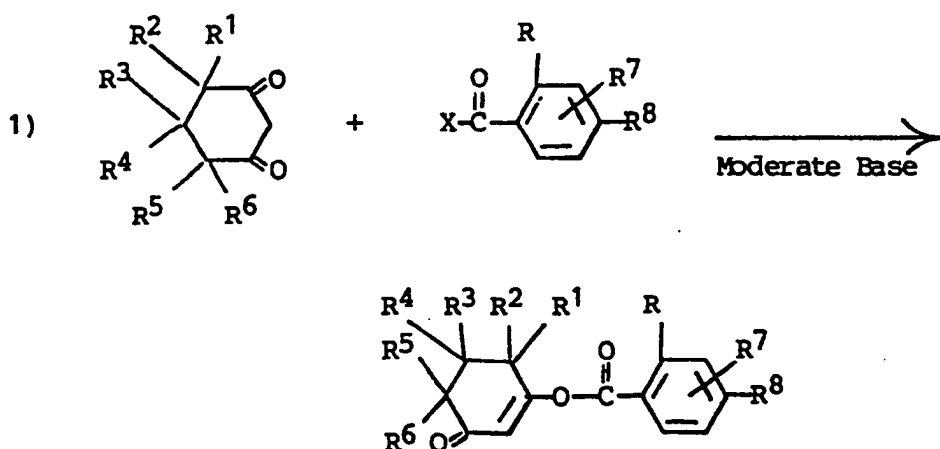
Examples of cations of these bases are inorganic cations such as alkali metals e.g. lithium, sodium, and potassium organic cations such as

substituted ammonium, sulfonium or phosphonium wherein the substituent is an aliphatic or aromatic group.

The compounds of this invention and their salts are active herbicides of a general type. That is, they are herbicidally effective against a wide range of plant species. The method of controlling undesirable vegetation of the present invention comprises applying an herbicidally effective amount of the above-described compounds to the area where control is desired.

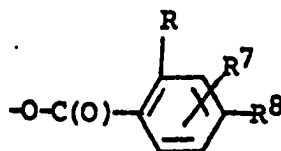
The compounds of the present invention can be prepared by the following two-step general method.

The process proceeds via the production of an enol ester intermediate as shown in reaction (1). The final product is obtained by rearrangement of the enol ester as shown in reaction (2). The two reactions may be conducted as separate steps by isolation and recovery of the enol ester using conventional techniques prior to conducting step (2), or by addition of a cyanide source to the reaction medium after the formation of the enol ester, or in one step by inclusion of the cyanide source at the start of reaction (1).



C<sub>1</sub>-C<sub>4</sub> alkyl-C(O)-O-, C<sub>1</sub>-C<sub>4</sub> alkoxy-C(O)-O- or

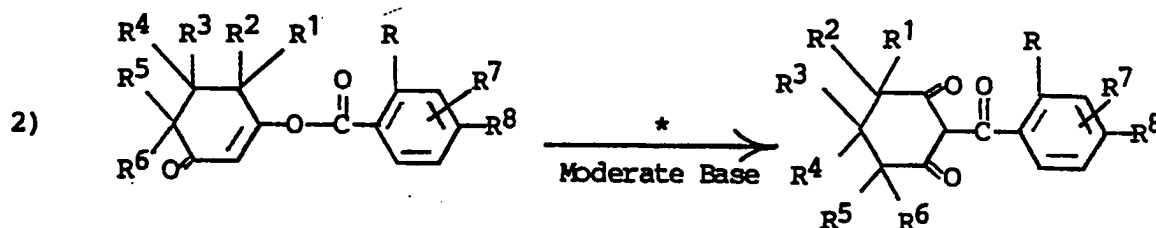
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wherein R, R<sup>7</sup> and R<sup>8</sup> in this portion of the molecule are identical with those in the reactant shown above and the moderate base is as defined, preferably tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, pyridine, alkali metal carbonate or alkali metal phosphate.

- 5 Generally, in step (1) mole amounts of the dione and substituted benzoyl reactant are used, along with a mole amount or excess of the base. The two reactants are combined in an organic solvent such as methylene chloride, toluene, ethyl acetate or dimethylformamide. The base or benzoyl reactant preferably are added to the reaction mixture with cooling.
- 10 The mixture is stirred at 0°C-50°C until the reaction is substantially complete.

The reaction product is worked up by conventional techniques.



\* = Cyanide source.

Moderate base = as defined herein.

wherein R through R<sup>8</sup> are as defined.

- Generally, in step (2) a mole of the enol ester intermediate is
- 15 reacted with 1 to 4 moles of the base, preferably about 2 moles of moderate base and from 0.01 mole to about 0.5 mole or higher, preferably around 0.1 mole of the cyanide source (e.g., potassium cyanide or acetone cyanohydrin). The mixture is stirred in a reaction pot until the rearrangement is substantially complete at a temperature below 80°C, preferably about
- 20 20°C to about 40°C, and the desired product is recovered by conventional techniques.

The term "cyanide source" refers to a substance or substances which under the rearrangement conditions consists of or generates hydrogen cyanide and/or cyanide anion.

The process is conducted in the presence of a catalytic amount  
5 of a source of cyanide anion and/or hydrogen cyanide, together with a molar excess, with respect to the enol ester, of a moderate base.

Preferred cyanide sources are alkali metal cyanides such as sodium and potassium cyanide; cyanohydrins of methyl alkyl ketones having from 1-4 carbon atoms in the alkyl groups, such as acetone or methyl iso-  
10 butyl ketone cyanohydrins; cyanohydrins of benzaldehyde or of C<sub>2</sub>-C<sub>5</sub> aliphatic aldehydes such as acetaldehyde, propionaldehyde, etc., cyanohydrins; zinc cyanide; tri(lower alkyl) silyl cyanides, notably trimethyl silyl cyanide; and hydrogen cyanide itself. Hydrogen cyanide is considered most advantageous as it produces relatively rapid reaction and  
15 is inexpensive. Among cyanohydrins the preferred cyanide source is acetone cyanohydrin.

The cyanide source is used in an amount up to about 50 mole percent based on the enol ester. It may be used in as little as about 1 mole percent to produce an acceptable rate of reaction at about 40°C on a small  
20 scale. Larger scale reactions give more reproducible results with slightly higher catalyst levels of about 2 mole percent. Generally about 1-10 mole % of the cyanide source is preferred.

The process is conducted with a molar excess, with respect to the enol ester, of a moderate base. By the term "moderate base" is meant  
25 a substance which acts as a base yet whose strength or activity as a base lies between that of strong bases such as hydroxides (which could cause hydrolysis of the enol ester) and that of weak bases such as bicarbonates (which would not function effectively). Moderate bases suitable for use in this embodiment include both organic bases such as tertiary amines and  
30 inorganic bases such as alkali metal carbonates and phosphates. Suitable tertiary amines include trialkylamines such as triethylamine, trialkanolamines such as triethanolamine, and pyridine. Suitable inorganic bases include potassium carbonate and trisodium phosphate.



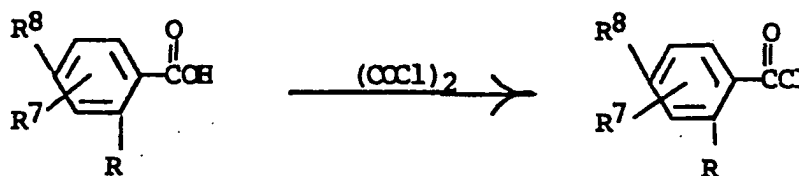
The base is used in an amount of from about 1 to about 4 moles per mole of enol ester, preferably about 2 moles per mole.

When the cyanide source is an alkali metal cyanide, particularly potassium cyanide, a phase transfer catalyst may be included in the reaction. Particularly suitable phase transfer catalysts are the Crown ethers.

A number of different solvents may be usable in this process, depending on the nature of the acid chloride or the acylated product. A preferred solvent for this reaction is 1,2-dichloroethane. Other solvents which may be employed, depending on the reactants or products include toluene, acetonitrile, methylene chloride, ethyl acetate, dimethylformamide, and methyl isobutyl ketone (MIBK).

In general, depending on the nature of the reactants and the cyanide source, the rearrangement may be conducted at temperatures up to about 50°C.

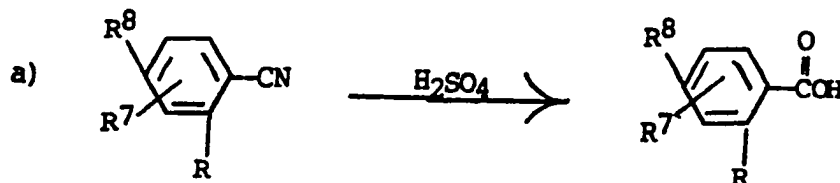
The above described substituted benzoyl chlorides can be prepared from the corresponding substituted benzoic acids according to the teaching of Reagents for Organic Synthesis, Vol. I, L.F. Fieser and M. Fieser, pp. 767-769 (1967).



wherein R, R<sup>7</sup> and R<sup>8</sup> are as previously defined.

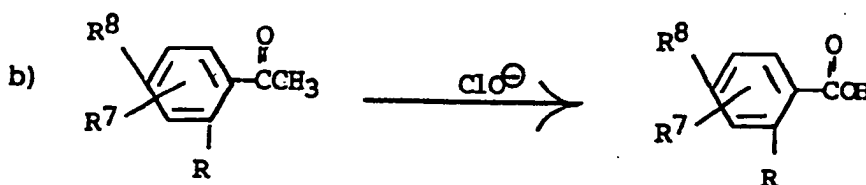
The substituted benzoic acids can be prepared by a wide variety of general methods according to the teaching of The Chemistry of Carboxylic Acids and Esters, S. Patai, editor, J. Wiley and Sons, New York, N.Y. (1969) and Survey of Organic Synthesis, C.A. Buehler and D.F. Pearson, J. Wiley and Sons, (1970).

The following are four representative examples of the methods described therein.



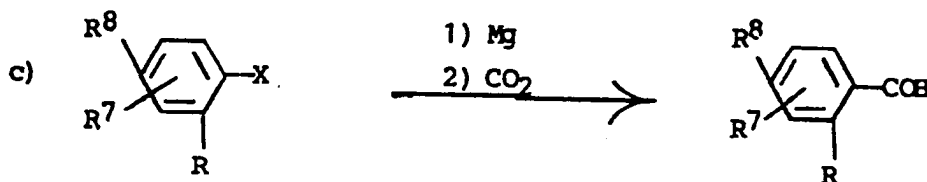
wherein R, R<sup>7</sup> and R<sup>8</sup> are as previously defined.

In reaction (a) the substituted benzonitrile is heated to reflux  
5 in aqueous sulfuric acid for several hours. The mixture is cooled and the reaction product is isolated by conventional techniques.



wherein R, R<sup>7</sup> and R<sup>8</sup> are as previously defined.

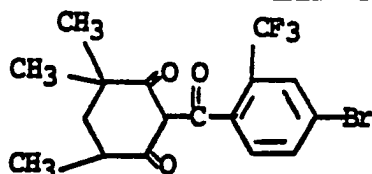
In reaction (b) the substituted acetophenone is heated to reflux  
for several hours in an aqueous hypochlorite solution. The mixture is  
10 cooled and the reaction product is isolated by conventional techniques.



wherein R, R<sup>7</sup> and R<sup>8</sup> are as defined and X is chlorine, bromine or iodine.

The substituted aromatic halide is allowed to react with magnesium in a solvent such as ether. The solution is then poured over crushed dry ice and the benzoic acid is isolated by conventional techniques.

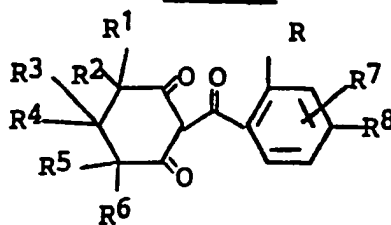
25 The following example teaches the synthesis of a representative compound of this invention.

EXAMPLE 12-(4'-Bromo-2'-trifluoromethylbenzoyl)-4,4,6-trimethyl-1,3-  
cyclohexanedione

4-Bromo-2-trifluoromethylbenzoyl chloride (4.3 g, 15 mmol) and 4,4,6-trimethyl-1,3-cyclohexanedione (2.3 g, 15 mmol) were dissolved in 100 ml methylene chloride. The solution was cooled with an ice bath and triethylamine (2.1 ml, 15 mmol) in 10 ml methylene chloride was added  
5 dropwise. The ice bath was then removed and the resulting solution stirred for 30 minutes at room temperature. The solution was washed with 2N hydrochloric acid (2N HCl), 5% potassium carbonate solution (5% K<sub>2</sub>CO<sub>3</sub>) and saturated sodium chloride solution (brine), dried over anhydrous magnesium sulfate (MgSO<sub>4</sub>) and concentrated under vacuum. The residue (5.1 g)  
10 was dissolved in 20 ml acetonitrile. Triethylamine (3.5 ml, 25 mmol) and 0.4 ml acetone cyanohydrin were added and the solution stirred for two hours at room temperature while protected by a drying tube (calcium sulfate). After dilution with ether, the solution was washed with 2N HCl and extracted with 5% K<sub>2</sub>CO<sub>3</sub>. The aqueous extract was acidified with concentrated hydrochloric acid and extracted with ether. The ether was washed  
15 with brine, dried (MgSO<sub>4</sub>) and concentrated under vacuum. The resulting oil was purified on a silica gel column (80:20:1 hexane:ethyl acetate:acetic acid - eluent), yielding 1.5 g of a viscous oil which was identified as the desired compound by nuclear magnetic resonance spectroscopy,  
20 infrared spectroscopy and mass spectroscopy.

The following is a table of certain selected compounds that are preparable according to the procedure described hereto. Compound numbers are assigned to each compound and are used throughout the remainder of the application.

TABLE I



Comp. No.	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	n <sub>D</sub> <sup>30</sup> or m.p.
1	CH <sub>3</sub>	H	H	H	H	H	H	H	H	35-42°C
2	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	47-53°C
3	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	Br	oil
4	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CN	oil
5	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-NO <sub>2</sub>	H	oil
6	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	5-Cl	H	oil
7	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CH <sub>3</sub> SO <sub>2</sub> -	oil
8	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CH <sub>3</sub> SO <sub>2</sub> -	oil
9	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-Cl	H	oil
10	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> -	oil
11	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> -	oil
12	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	n-C <sub>3</sub> H <sub>7</sub> SO <sub>2</sub> -	oil
13	CH <sub>3</sub>	H	H	H	H	H	H	H	CH <sub>3</sub> SO <sub>2</sub> -	oil
14	CH <sub>3</sub>	H	H	H	H	H	H	H	n-C <sub>3</sub> H <sub>7</sub> SO <sub>2</sub> -	oil
15	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CH <sub>3</sub> S-	oil
16	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	Br	oil
17	CH <sub>3</sub>	H	H	H	H	H	H	H	CN	oil
18	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	F	oil
19	CH <sub>3</sub>	H	H	H	H	H	H	H	C <sub>2</sub> H <sub>5</sub> -SO <sub>2</sub> -	oil
20	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	H	65-67°C
21	CH <sub>3</sub>	H	H	H	H	H	H	3-I	H	oil
22	CH <sub>3</sub>	H	H	H	H	H	H	3-NO <sub>2</sub>	H	oil
23	CH <sub>3</sub>	H	H	H	H	H	H	3-CN	H	96-101°C
24	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	H	oil
25	CF <sub>3</sub>	H	H	H	H	H	H	H	H	oil
26	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	Br	oil
27	CF <sub>3</sub>	H	H	H	H	H	H	H	Cl	82-88°C
28	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	Cl	oil
29	CF <sub>3</sub>	H	H	H	H	H	H	H	C <sub>2</sub> H <sub>5</sub> S-	oil

TABLE I  
(continued)

Comp. No.	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	R <sup>7</sup>	R <sup>8</sup>	$n_D^{30}$ or m.p.
30	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> -	oil
31	CF <sub>3</sub>	H	H	H	H	H	H	H	CN	oil
32	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CN	oil
33a	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	Br	oil
34	CH <sub>3</sub>	H	H	H	H	H	H	H	CH <sub>3</sub>	
35	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-Cl	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub>	115-117°C
36	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub>	oil
37	CH <sub>3</sub>	b)	b)	H	H	H	H	3-CF <sub>3</sub>	H	oil
38	CH <sub>3</sub>	c)	H	i-C <sub>3</sub> H <sub>7</sub>	H	H	H	3-NO <sub>2</sub>	H	88-108°C
39	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CH <sub>3</sub> S	oil
40	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CH <sub>3</sub> S	oil
41	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CH <sub>3</sub> SO <sub>2</sub> -	oil
42	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CF <sub>3</sub>	oil
43	CH <sub>3</sub>	H	H	H	H	H	H	H	CF <sub>3</sub>	114-120°C
44	CH <sub>3</sub>	H	H	H	H	H	H	3-Cl	Cl	oil
45	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-Cl	Cl	oil
46	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	3-CF <sub>3</sub>	H	oil
47	CF <sub>3</sub>	H	H	H	H	H	H	H	CH <sub>3</sub> S	oil
48	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	CF <sub>3</sub>	oil
49	CF <sub>3</sub>	H	H	H	H	H	H	H	CF <sub>3</sub>	oil
50	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	H	H	CF <sub>3</sub>	oil
51	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	H	H	CH <sub>3</sub> SO <sub>2</sub>	oil
52	CF <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	H	H	CH <sub>3</sub>	H	H	C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub>	oil
53	CH <sub>3</sub>	H	H	H	H	H	H	H	Br	94-98°C
54	CH <sub>3</sub>	H	H	H	H	H	H	d)	H	oil

a) Prepared in Example 1.

b) -(CH<sub>2</sub>)<sub>5</sub>-

c) C<sub>2</sub>H<sub>5</sub>OC(O)-

d) 3-N(CH<sub>3</sub>)COCH<sub>3</sub>

### Herbicidal Screening Tests

As previously mentioned, the herein described compounds produced in the above-described manner are phytotoxic compounds which are useful and valuable in controlling various plant species. Selected compounds of this invention were tested as herbicides in the following manner.

- 5            Pre-emergence herbicide test. On the day preceding treatment, seeds of eight different weed species are planted in loamy sand soil in individual rows using one species per row across the width of a flat. The weeds used are green foxtail (FT) (Setaria viridis), watergrass (WG) (Echinochloa crusgalli), wild oat (WO) (Avena fatua), annual morningglory (AMG) (Ipomoea lacunosa), velvetleaf (VL) (Abutilon theophrasti), Indian  
10 mustard (MD) (Brassica juncea), curly dock (CD) (Rumex crispus), and yellow nutsedge (YNG) (Cyperus esculentus). Ample seeds are planted to give about 20 to 40 seedlings per row, after emergence, depending upon the size of the plants.
- 15            Using an analytical balance, 600 milligrams (mg) of the compound to be tested are weighed out on a piece of glassine weighing paper. The paper and compound are placed in a 60 milliliter (ml) wide-mouth clear bottle and dissolved in 45 ml of acetone or substituted solvent. Eighteen  
20 ml of this solution are transferred to a 60 ml wide-mouth clear bottle and diluted with 22 ml of a water and acetone mixture (19:1) containing enough polyoxyethylene sorbitan monolaurate emulsifier to give a final solution of 0.5% (v/v). The solution is then sprayed on a seeded flat on a linear spray table calibrated to deliver 80 gallons per acre (748 L/ha). The application rate is 4 lb/acre (4.48 Kg/ha).
- 25            After treatment, the flats are placed in the greenhouse at a temperature of 70 to 80°F and watered by sprinkling. Two weeks after treatment, the degree of injury or control is determined by comparison with untreated check plants of the same age. The injury rating from 0 to 100% is recorded for each species as percent control with 0% representing  
30 no injury and 100% representing complete control.

The results of the tests are shown in the following Table II.

TABLE II

Pre-Emergence Herbicidal Activity  
Application Rate -- 4.48 kg/ha

<u>Cmpd.</u> <u>No.</u>	<u>FT</u>	<u>WG</u>	<u>WO</u>	<u>AMG</u>	<u>VL</u>	<u>MD</u>	<u>CD</u>	<u>YNG</u>
1	40	20	0	0	0	0	0	100
2	60	70	0	0	0	0	90	100
3	100	100	50	50	100	100	85	90
4	100	100	90	30	100	85	95	95
5	100	100	80	10	100	100	100	95
6	20	35	25	15	90	85	40	85
7	100	100	90	100	100	100	100	95
8	100	100	90	100	100	100	100	95
9	100	100	0	0	100	80	100	90
10	100	100	100	100	100	100	100	95
11	100	100	70	100	100	100	97	95
12	100	100	60	100	100	100	100	95
13	100	100	60	100	100	100	100	95
14	80	100	50	80	100	100	90	90
15	100	100	80	100	100	100	100	-
16	50	75	0	25	100	100	95	60
17	100	100	40	100	100	100	100	85
18	100	100	0	20	100	100	80	70
20	70	75	0	25	100	95	100	60
21	50	60	0	0	100	80	80	60
22	100	95	35	25	100	100	90	50
23	95	100	40	20	100	100	90	50
24	100	100	90	0	45	85	80	90
25	100	100	25	60	100	100	100	75
34	35	40	10	0	60	25	0	70
37	50	60	0	0	60	0	50	0
38	35	40	0	0	0	0	0	0
52	85	100	30	95	100	100	-	80
53	100	100	0	85	100	100	-	80
54	100	100	90	25	100	100	-	80

A blank (-) indicates that the weed was not tested.

Post-Emergence Herbicide Test: This test is conducted in an identical manner to the testing procedure for the pre-emergence herbicide test, except the seeds of the eight different weed species are planted 10-12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence herbicide test are reported in Table III.

TABLE III  
Post-Emergence Herbicidal Activity  
Application Rate — 4.48 kg/ha

<u>Cmpd.</u> <u>No.</u>	<u>FT</u>	<u>WG</u>	<u>WO</u>	<u>AMG</u>	<u>VL</u>	<u>MD</u>	<u>CD</u>	<u>YNG</u>
1	60	40	20	30	40	40	50	60
2	50	40	10	20	20	20	40	60
3	100	100	85	100	100	100	100	75
4	100	100	95	85	100	95	100	60
5	95	95	100	65	90	25	70	45
6	40	30	0	20	90	25	20	70
7	100	100	100	100	100	100	100	90
8	100	95	100	100	100	100	100	70
9	65	65	0	20	80	65	90	80
10	100	100	100	100	100	100	100	70
11	85	90	90	85	90	80	30	60
12	100	90	65	80	100	100	100	50
13	100	95	100	100	100	100	90	-
14	100	100	100	100	100	100	100	50
15	25	35	15	30	80	25	20	0
16	100	85	70	75	90	90	50	-
17	100	100	100	100	100	100	100	-
18	90	85	85	85	90	95	70	40
20	40	60	10	60	100	100	100	50
21	35	60	10	60	100	100	80	60
22	95	95	35	100	100	100	90	50
23	100	100	40	100	100	100	90	50
24	100	75	100	60	-	100	100	60
25	95	95	90	95	100	100	95	35
34	50	40	0	35	50	70	30	50
37	20	60	0	30	30	50	50	50
38	25	50	0	25	25	50	20	20
52	0	60	50	50	10	50	-	20
53	0	50	0	50	50	50	-	30
54	90	75	60	50	50	80	-	80

A blank (-) indicates the weed was not tested.

Pre-Emergence Multi-Weed Herbicide Test

Several compounds were evaluated at an application rate of 1 or 1/2 lb/acre (1.12 or 0.56 kg/ha) for pre-emergence activity against a larger number of weed species.



Pre-Emergence Multi-Weed Herbicide Test

Several compounds were evaluated at an application rate of 1 or 1/2 lb/acre (1.12 or 0.56 kg/ha) for pre-emergence activity against a larger number of weed species.

The process was generally similar to the pre-emergence herbicide test described above except that only 150 or 75 milligrams of test compound were weighed out and the application rate was 40 gallons per acre.

Redroot pigweed (PW) and curly dock (CD) were eliminated in this test and the following weed species were added:

10	<u>Grasses:</u>	downy brome	<u>Bromus tectorum</u>	(DB)
		annual ryegrass	<u>Lolium multiflorum</u>	(ARG)
		Johnsongrass	<u>Sorghum halepense</u>	(JG)
		broadleaf signalgrass	<u>Brachiaria platyphylla</u>	(BSG)
		hemp sesbania	<u>Sesbania exaltata</u>	(SESB)
		sicklepod	<u>Cassia obtusifolia</u>	(SP)
		cocklebur	<u>Xanthium sp.</u>	(CB)

The results of the test are shown in Tables IV and V.

TABLE IV  
Pre-Emergence Multi-weed Herbicide Test  
 Application Rate - 1.12 kg/ha

Ompd.	No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
	19	40	35	60	100	90	30	90	100	100	-	20	100	90	-
	26	25	70	45	95	60	25	85	35	75	-	20	100	95	90
	27	45	65	40	100	60	25	80	100	85	100	40	100	95	35
	28	80	100	90	100	100	90	100	70	90	100	30	100	95	35
	29	90	45	75	100	85	40	90	95	90	100	40	100	95	-
	30	90	95	80	100	90	75	100	100	80	100	60	100	95	-
	31	60	65	75	100	100	55	95	100	100	100	100	100	95	-
	32	90	100	90	100	100	65	85	100	90	100	95	100	85	-
	33	100	100	95	100	100	95	100	100	100	100	25	100	90	-
	35	90	100	100	100	-	90	90	100	90	100	10	100	75	-
	36	90	35	85	100	-	15	80	95	90	100	50	100	95	-
	39	100	100	100	100	100	95	100	100	100	100	100	100	98	-
	40	100	100	80	100	100	70	100	100	100	100	90	100	95	-
	41	100	100	100	100	100	100	100	100	100	100	60	100	98	-
	42	60	100	85	100	100	70	95	100	95	100	10	100	95	50
	43	85	100	25	100	60	25	98	100	100	100	100	100	90	100
	44	0	80	10	85	0	0	75	0	30	100	0	100	0	10
	45	25	100	40	100	60	0	65	60	60	100	50	100	70	0
	50	-	100	50	100	35	35	75		100	100	-			

(-) = Not tested.

TABLE V  
Pre-Emergence Multi-weed Herbicide Test  
 Application Rate - 0.56 kg/ha

Ompd.	No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
	46	0	65	35	75	65	0	0	0	35	100	25	90	80	0
	47	-	60	35	100	100	0	90	100	100	100	70	-	100	75
	48	-	75	20	90	60	0	15	70	35	90	0	-	20	40
	49	-	60	10	100	60	0	50	100	95	100	40	-	90	100
	51	-	40	10	95	40	10	50	65	100	100	0	-	95	65

(-) - Not tested.

Post-Emergence Multi-Weed Herbicide Test: This test is conducted in an identical manner to the testing procedure for the post-emergence herbicide test, except the seeds of the eight weed species used in the pre-emergence multi-weed herbicide test were used and the seeds

were planted 10-12 days before treatment. Also, watering of the treated flats is confined to the soil surface and not to the foliage of the sprouted plants.

The results of the post-emergence multi-weed herbicide test are reported in Table VI and VII.

TABLE VI  
Post-Emergence Multi-Weed Herbicidal Activity  
Application Rate — 2.24 kg/ha

Cmpd. No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
19	100	90	65	100	100	98	100	100	100	100	60	100	70	100
26	60	75	60	95	45	50	90	50	90	100	40	90	60	-
27	80	70	65	95	100	90	100	100	100	100	85	100	75	-
28	80	100	75	90	85	80	100	80	80	100	30	100	85	85
29	85	70	55	90	98	90	100	100	100	100	35	100	60	100
30	90	80	40	90	85	80	80	70	100	100	20	100	40	-
31	100	80	20	100	100	100	100	100	100	100	100	100	85	-
32	70	90	60	100	100	98	100	100	100	100	100	100	60	-
33	95	100	80	100	90	100	100	100	100	100	70	100	40	-
35	70	90	40	100	-	100	100	100	100	100	98	100	30	-
36	85	100	35	100	-	20	100	100	100	100	100	100	15	-
39	100	100	85	100	100	100	100	100	100	100	100	100	90	100
40	100	100	30	100	100	100	100	100	100	100	90	100	75	-
41	100	100	35	90	70	100	90	100	100	100	50	100	70	-
42	45	100	50	100	70	55	80	100	100	100	70	100	75	100
43	25	80	15	98	35	0	20	100	100	100	100	100	60	95
44	0	15	0	65	0	0	0	70	100	100	40	100	0	100
45	0	75	35	70	35	0	60	50	85	100	50	100	75	70
50	-	40	0	75	45	40	60	100	100	95	30	-	60	100

(-) = Not tested.

TABLE VII

Post-Emergence Multi-Weed Herbicidal Activity  
Application Rate — 0.56 kg/ha

Cmpd. No.	DB	FT	ARG	WG	JG	WO	BSG	AMG	SESB	VL	SP	MD	YNG	CB
46	25	35	20	50	35	35	0	20	75	100	35	95	-	50
47	-	75	25	90	40	25	80	100	100	100	80	-	75	100
48	-	50	35	80	35	40	0	75	100	85	15	-	50	75
49	-	35	0	75	30	0	20	100	100	100	80	-	25	85
51	-	35	0	80	35	20	70	50	95	95	25	-	65	50

(-) = Not Tested.

The compounds of the present invention are useful as herbicides and can be applied in a variety of ways at various concentrations. In practice, the compounds herein defined are formulated into herbicidal compositions, by admixture, in herbicidally effective amounts, with the adju-  
 5 vants and carriers normally employed for facilitating the dispersion of active ingredients for agricultural applications, recognizing the fact that the formulation and mode of application of a toxicant may affect the activity of the materials in a given application. Thus, these active herbicidal compounds may be formulated as granules of relatively large  
 10 particle size, as wettable powders, as emulsifiable concentrates, as powdery dusts, as solutions or as any of several other known types of formulations, depending upon the desired mode of application. Preferred formulations for pre-emergence herbicidal applications are wettable pow-  
 15 ders, emulsifiable concentrates and granules. These formulations may contain as little as about 0.5% to as much as about 95% or more by weight of active ingredient. A herbicidally effective amount depends upon the nature of the seeds or plants to be controlled and the rate of application varies from about 0.05 to approximately 25 pounds per acre, preferably from about 0.1 to about 10 pounds per acre.

20 Wettable powders are in the form of finely divided particles which disperse readily in water or other dispersants. The wettable powder is ultimately applied to the soil either as a dry dust or as a dispersion in water or other liquid. Typical carriers for wettable powders include fuller's earth, kaolin clays, silicas and other readily wet organic or  
 25 inorganic diluents. Wettable powders normally are prepared to contain about 5% to about 95% of the active ingredient and usually also contain a

small amount of wetting, dispersing, or emulsifying agent to facilitate wetting and dispersion.

Emulsifiable concentrates are homogeneous liquid compositions which are dispersible in water or other dispersant, and may consist  
5 entirely of the active compound with a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthal, isophorone and other non-volatile organic solvents. For herbicidal application, these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The  
10 percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises about 0.5% to 95% of active ingredient by weight of the herbicidal composition.

Granular formulations wherein the toxicant is carried on relatively coarse particles, are usually applied without dilution to the area  
15 in which suppression of vegetation is desired. Typical carriers for granular formulations include sand, fuller's earth, bentonite clays, vermiculite, perlite and other organic or inorganic materials which absorb or which may be coated with the toxicant. Granular formulations normally are  
20 prepared to contain about 5% to about 25% of active ingredients which may include surface-active agents such heavy aromatic naphthas, kerosene or other petroleum fractions, or vegetable oils; and/or stickers such as destrins, glue or synthetic resins.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, for example, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; polyhydric alcohols; and  
25 other types of surface-active agents, many of which are available in commerce. The surface-active agent, when used, normally comprises from 0.1% to 15% by weight of the herbicidal composition.

30 Dusts, which are free-flowing admixtures of the active ingredient with finely divided solids such as talc, clays, flours and other organic and inorganic solids which act as dispersants and carriers for the toxicant, are useful formulations for soil-incorporating application.

Pastes, which are homogeneous suspensions of a finely divided solid toxicant in a liquid carrier such as water or oil, are employed for specific purposes. These formulations normally contain about 5% to about 95% of active ingredient by weight, and may also contain small amounts of a wetting, dispersing or emulsifying agent to facilitate dispersion. For application, the pastes are normally diluted and applied as a spray to the area to be affected.

Other useful formulations for herbicidal applications include simple solutions of the active ingredient in a dispersant in which it is completely soluble at the desired concentration, such as acetone, alkylated naphthalenes, xylene and other organic solvents. Pressurized sprays, typically aerosols, wherein the active ingredient is dispersed in finely-divided form as a result of vaporization of a low boiling dispersant solvent carrier, such as the Freons, may also be used.

The phytotoxic compositions of this invention are applied to the plants in the conventional manner. Thus, the dust and liquid compositions can be applied to the plant by the use of power-dusters, boom and hand sprayers and spray dusters. The compositions can also be applied from airplanes as a dust or a spray because they are effective in very low dosages. In order to modify or control growth of germinating seeds or emerging seedlings, as a typical example, the dust and liquid compositions are applied to the soil according to conventional methods and are distributed in the soil to a depth of at least 1/2 inch below the soil surface. It is not necessary that the phytotoxic compositions be admixed with the soil particles since these compositions can also be applied merely by spraying or sprinkling the surface of the soil. The phytotoxic compositions of this invention can also be applied by addition to irrigation water supplied to the field to be treated. This method of application permits the penetration of the compositions into the soil as the water is absorbed therein. Dust compositions, granular compositions or liquid formulations applied to the surface of the soil can be distributed below the surface of the soil by conventional means such as discing, dragging or mixing operations.

EMULSIFIABLE CONCENTRATE FORMULATIONSGeneral Formula with Ranges

Herbicidal compound	5-55
surfactant(s)	5-25
solvent(s)	20-90
	<u>100%</u>

Specific Formula

herbicidal compound	54
proprietary blend of oil-soluble sulfonates and polyoxyethylene ethers	10
polar solvent	27
petroleum hydrocarbon	9
	<u>100%</u>

WETTABLE POWDER FORMULATIONS

herbicidal compound	3-90
wetting agent	0.5-2
dispersing agent	1-8
diluent(s)	8.5-87
	<u>100%</u>

herbicidal compound	80
sodium dialkyl naphthalene sulfonate	0.5
sodium lignosulfonate	7
attapulgitic clay	12.5
	<u>100%</u>

EXTRUDED GRANULAR FORMULATIONS

herbicidal compound	1-20
binding agent	0-10
diluent(s)	70-99
	<u>100%</u>

herbicidal compound	10
lignin sulfonate	5
calcium carbonate	85
	<u>100%</u>

FLOWABLE FORMULATIONS

herbicidal compound	20-70
surfactant(s)	1-10
suspending agent(s)	0.05-1
antifreeze agent	1-10
antimicrobial agent	1-10
antifoam agent	0.1-1
solvent	7.95-77.85
	<u>100%</u>

herbicidal compound	45
polyoxyethylene ether	5
attagel	0.05
propylene glycol	10
BIT	0.03
silicone defoamer	0.02
water	39.9
	<u>100%</u>

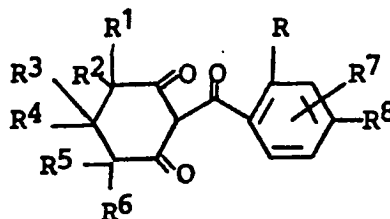
The phytotoxic compositions of this invention can also contain other additaments, for example, fertilizers and other herbicides, pesticides and the like, used as adjuvant or in combination with any of the above-described adjuvants. Other phytotoxic compounds useful in combination with the above-described compounds include, for example, anilides

such as 2-benzothiazole-2-yloxy-N-methyl acetanilide, 2-chloro-2',6'-dimethyl-N-(n-propylethyl) acetanilide, 2-chloro-2',6'-diethyl-N-(butoxymethyl) acetanilide; 2,4-dichlorophenoxyacetic acids, 2,4,5-trichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives, such as 2,4-bis(3-methoxypropylamino)-6-methylthio-s-triazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine, and 2-ethylamino-4-isopropylamino-6-methyl-mercapto-s-triazine; urea derivatives, such as 3-(3,5-dichlorophenyl)-1,1-dimethylurea and 3-(p-chlorophenyl)-1,1-dimethylurea; and acetamides such as N,N-diallyl- $\alpha$ -chloroacetamide, and the like; benzoic acids such as 3-amino-2,5-dichlorobenzoic acid; thiocarbamates such as S-(1,1-dimethylbenzyl)-piperidine-1-carbothioate, 3-(4-chlorophenyl)-methyl diethylcarbothioate, ethyl-1-hexahydro-1,4-azepine-1-carbothioate, S-ethyl-hexahydro-1H-azepine-1-carbothioate, S-propyl N,N-dipropylthiocarbamate, S-ethyl N,N-dipropylthiocarbamate, S-ethyl cyclohexylethylthiocarbamate and the like; anilines such as 4-(methylsulfonyl)-2,6-dinitro-N,N-substituted aniline, 4-trifluoromethyl-2,6-dinitro-N,N-di-n-propyl aniline, 4-trifluoromethyl-2,6-dinitro-N-ethyl-N-butyl aniline, 2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid, 2-[1-(ethoxyimino)butyl]-5-[2-ethylthio)propyl]-3-hydroxy-2-cyclohexene-1-one, (+)-butyl-2[4-[(5-trifluoromethyl)-2-pyridinyl)oxy]phenoxy]propanate, sodium 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate, 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-2,2-dioxide, and 4-amino-6-tert-butyl-3(methylthio)-as-triazin-5(4H)-one or 4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one and S-(O,O-diisopropyl)-benzene sulfonamide. Fertilizers useful in combination with the active ingredients include, for example, ammonium nitrate, urea and superphosphate. Other useful additaments include materials in which plant organisms take root and grow such as compost, manure, humus, sand, and the like.



## WHAT IS CLAIMED IS:

## 1. A compound of the formula



wherein

R is C<sub>1</sub>-C<sub>4</sub> alkyl optionally substituted with halogen;R<sup>1</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

5 R<sup>2</sup> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl or R<sup>a</sup>-O-C(=O)- wherein R<sup>a</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl; or

R<sup>1</sup> and R<sup>2</sup> together are alkylene having 3 to 6 carbon atoms;R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;R<sup>4</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

10 R<sup>5</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl;

R<sup>6</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; and

R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9) R<sup>b</sup>SO<sub>n</sub>- wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or

15 (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>e</sup>C(O)- wherein R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined, with the proviso that R<sup>7</sup> is not attached to the 6-position.

20 2. The compounds of Claim 1 wherein R is methyl or CF<sub>3</sub>; R<sup>1</sup> is hydrogen or methyl; R<sup>2</sup> is hydrogen or methyl; R<sup>3</sup> is hydrogen or methyl; R<sup>4</sup> is hydrogen or methyl; R<sup>5</sup> is hydrogen or methyl; R<sup>6</sup> is hydrogen or methyl; R<sup>7</sup> and R<sup>8</sup> independently are (1) hydrogen; (2) halogen; (3) C<sub>1</sub>-C<sub>4</sub> alkyl; (4) C<sub>1</sub>-C<sub>4</sub> alkoxy; (5) OCF<sub>3</sub>; (6) cyano; (7) nitro; (8) C<sub>1</sub>-C<sub>4</sub> haloalkyl; (9)

25 R<sup>b</sup>SO<sub>n</sub>- wherein n is the integer 0, 1 or 2; and R<sup>b</sup> is (a) C<sub>1</sub>-C<sub>4</sub> alkyl; (b) C<sub>1</sub>-C<sub>4</sub> alkyl substituted with halogen or cyano; (c) phenyl; or (d) benzyl; (10) -NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> independently are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>e</sup>C(O)- wherein R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NR<sup>c</sup>R<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined.

3. The compounds of Claim 2 wherein  $R^7$  and  $R^8$  are independently are hydrogen; chlorine; fluorine; bromine; methyl; methoxy;  $OCF_3$ ; cyano; nitro; trifluoromethyl;  $R^bSO_n$ - wherein  $n$  is the integer 2 and  $R^b$  is methyl, chloromethyl, trifluoromethyl, cyanomethyl, ethyl, or  $n$ -propyl;
- 5 - $NR^cR^d$  wherein  $R^c$  and  $R^d$  independently are hydrogen or  $C_1$ - $C_4$  alkyl;  $R^eC(O)$ - where  $R^e$  is  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy or  $SO_2NR^cR^d$  wherein  $R^c$  and  $R^d$  are as defined and  $R^7$  is in the 3-position.
4. The compound of Claim 2 wherein  $R^7$  is hydrogen and  $R^8$  is hydrogen, chlorine, bromine, fluorine,  $CF_3$  or  $R^bSO_2$  wherein  $R^b$  is  $C_1$ - $C_4$
- 10 alkyl.
5. The compound of Claim 2 wherein  $R$  is methyl;  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $CH_3SO_2$ -
6. The compound of Claim 2 wherein  $R$  is methyl;  $R^1$  is methyl;
- 15  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is methyl;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $CH_3SO_2$ -.
7. The compound of Claim 2 wherein  $R$  is methyl;  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $C_2H_5SO_2$ -.
- 20 8. The compound of Claim 2 wherein  $R$  is methyl;  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is  $CH_3SO_2$ -.
9. The compound of Claim 2 wherein  $R$  is methyl;  $R^1$  is methyl;  $R^2$  is methyl;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydro-
- 25 gen;  $R^7$  is hydrogen; and  $R^8$  is methylthio.
10. The compound of Claim 2 wherein  $R$  is methyl;  $R^1$  is hydrogen;  $R^2$  is hydrogen;  $R^3$  is hydrogen;  $R^4$  is hydrogen;  $R^5$  is hydrogen;  $R^6$  is hydrogen;  $R^7$  is hydrogen; and  $R^8$  is cyano.

11. The compound of Claim 2 wherein R is methyl; R<sup>1</sup> is hydrogen; R<sup>2</sup> is hydrogen; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is C<sub>2</sub>H<sub>5</sub>SO<sub>2</sub>-.

12. The compound of Claim 2 wherein R is CF<sub>3</sub>; R<sup>1</sup> is methyl; R<sup>2</sup> is methyl; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is methyl; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is bromine.

13. The compound of Claim 2 wherein R is methyl; R<sup>1</sup> is hydrogen; R<sup>2</sup> is hydrogen; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is 3-cyano; and R<sup>8</sup> is hydrogen.

14. The compound of Claim 2 wherein R is CF<sub>3</sub>; R<sup>1</sup> is methyl; R<sup>2</sup> is methyl; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is methyl; R<sup>6</sup> is hydrogen; R<sup>7</sup> is hydrogen; and R<sup>8</sup> is bromine.

15. The compound of Claim 2 wherein R is methyl; R<sup>1</sup> is methyl; R<sup>2</sup> is methyl; R<sup>3</sup> is hydrogen; R<sup>4</sup> is hydrogen; R<sup>5</sup> is hydrogen; R<sup>6</sup> is hydrogen; R<sup>7</sup> is 3-nitro; and R<sup>8</sup> is hydrogen.

16. The compounds of Claim 2 wherein R<sup>7</sup> is hydrogen.

17. The compounds of Claim 3 wherein R<sup>7</sup> is hydrogen.

18. The compound of Claim 1 wherein R<sup>1</sup> and R<sup>2</sup> are hydrogen or both methyl.

19. The compound of Claim 18 wherein R<sup>8</sup> is -SO<sub>2</sub>CH<sub>3</sub>, -SO<sub>2</sub>CH<sub>2</sub>Cl, CF<sub>3</sub>, -SO<sub>2</sub>CH<sub>3</sub>, cyano, -SO<sub>2</sub>CH<sub>2</sub>Cl or -SO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>.

20. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidally effective amount of a compound from Claims 1-19.

21. An herbicidal composition comprising an herbicidally active 2-(2-substituted benzoyl)-1,3-cyclohexanedione and an inert carrier therefor wherein the 2-benzoyl substituent is C<sub>1</sub>-C<sub>4</sub> alkyl optionally substituted with halogen.

22. The herbicidal composition of Claim 21 wherein the 2-(2-substituted benzoyl)-1,3-cyclohexanedione is a compound of Claims 1-19.

23. The method of controlling undesirable vegetation comprising applying to the area where control is desired, an herbicidal composition  
5 comprising an herbicidally active 2-(2-benzoyl)-1,3-cyclohexanedione and an inert carrier therefor wherein the 2-position of the benzoyl moiety is substituted with C<sub>1</sub>-C<sub>4</sub> alkyl, optionally substituted with halogen.

24. The method of Claim 23 wherein the 2-(2-benzoyl)-1,3-cyclohexanedione has a C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl or C<sub>1</sub>-C<sub>4</sub> haloalkylsulfonyl  
10 substitution on the phenyl ring.

25. The method of Claim 24 wherein said alkylsulfonyl or haloalkylsulfonyl substitution is at the 4-position of the phenyl ring.

26. The herbicidal composition of Claim 21 wherein the 2-(2-benzoyl)-1,3-cyclohexanedione has a C<sub>1</sub>-C<sub>4</sub> alkylsulfonyl or C<sub>1</sub>-C<sub>4</sub> haloalkylsulfonyl substitution on the phenyl ring.  
15

27. The herbicidal composition of Claim 25 wherein said alkylsulfonyl or haloalkylsulfonyl substitution is at the 4-position of the phenyl ring.

28. The method of Claim 23 wherein the 2-(2-benzoyl)-1,3-cyclohexanedione has a C<sub>1</sub>-C<sub>4</sub> haloalkyl substitution on the phenyl ring.  
20

29. The method of Claim 28 wherein said haloalkyl substitution is at the 4-position on the phenyl ring.

30. The herbicidal composition of Claim 21 wherein the 2-(2-benzoyl)-1,3-cyclohexanedione has a C<sub>1</sub>-C<sub>4</sub> haloalkyl substitution on the phenyl ring.  
25

31. The herbicidal composition of Claim 30 wherein said haloalkyl substitution is at the 4-position of the phenyl ring.

32. The herbicidal composition of Claim 30 wherein said haloalkyl is  $\text{CF}_3$ .

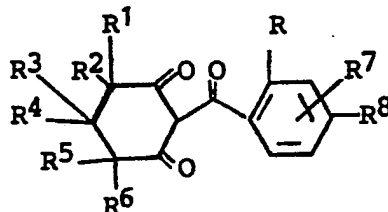
33. The method of Claim 20 wherein  $\text{R}^1$  and  $\text{R}^2$  are hydrogen or both methyl.

5 34. The method of Claim 33 wherein  $\text{R}^8$  is  $-\text{SO}_2\text{CH}_3$ ,  $-\text{SO}_2\text{CH}_2\text{Cl}$ ,  $\text{CF}_3$ ,  $-\text{SO}_2\text{CH}_3$ , cyano,  $-\text{SO}_2\text{CH}_2\text{Cl}$  or  $-\text{SO}_2\text{C}_2\text{H}_5$ .

35. The composition of matter of Claim 22 wherein  $\text{R}^1$  and  $\text{R}^2$  are hydrogen or both methyl.

36. The composition of matter of Claim 35 wherein  $\text{R}^8$  is  $-\text{SO}_2\text{CH}_3$ ,  
10  $-\text{SO}_2\text{CH}_2\text{Cl}$ ,  $\text{CF}_3$ ,  $-\text{SO}_2\text{CH}_3$ , cyano,  $-\text{SO}_2\text{CH}_2\text{Cl}$  or  $-\text{SO}_2\text{C}_2\text{H}_5$ .

37. A process for preparing a compound of the formula



wherein

$\text{R}$  is  $\text{C}_1$ - $\text{C}_4$  alkyl, optionally substituted with halogen;

$\text{R}^1$  is hydrogen or  $\text{C}_1$ - $\text{C}_4$  alkyl;

15  $\text{R}^2$  is hydrogen,  $\text{C}_1$ - $\text{C}_4$  alkyl or  $\text{R}^a\text{-O-C}(=\text{O})$ - wherein  $\text{R}^a$  is  $\text{C}_1$ - $\text{C}_4$  alkyl; or

$\text{R}^1$  and  $\text{R}^2$  together are alkylene having 3 to 6 carbon atoms;

$\text{R}^3$  is hydrogen or  $\text{C}_1$ - $\text{C}_4$  alkyl;

$\text{R}^4$  is hydrogen or  $\text{C}_1$ - $\text{C}_4$  alkyl;

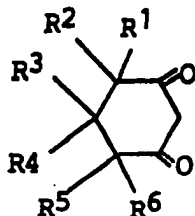
20  $\text{R}^5$  is hydrogen or  $\text{C}_1$ - $\text{C}_4$  alkyl;

$\text{R}^6$  is hydrogen or  $\text{C}_1$ - $\text{C}_4$  alkyl; and

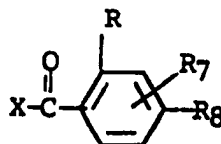
$\text{R}^7$  and  $\text{R}^8$  independently are (1) hydrogen; (2) halogen; (3)  $\text{C}_1$ - $\text{C}_4$  alkyl; (4)  $\text{C}_1$ - $\text{C}_4$  alkoxy; (5)  $\text{OCF}_3$ ; (6) cyano; (7) nitro; (8)  $\text{C}_1$ - $\text{C}_4$  halo-alkyl; (9)  $\text{R}^b\text{SO}_n$ - wherein  $n$  is the integer 0, 1 or 2; and  $\text{R}^b$  is (a)  $\text{C}_1$ - $\text{C}_4$  alkyl; (b)  $\text{C}_1$ - $\text{C}_4$  alkyl substituted with halogen or cyano; (c) phenyl; or  
25 (d) benzyl; (10)  $-\text{NR}^c\text{R}^d$  wherein  $\text{R}^c$  and  $\text{R}^d$  independently are hydrogen or

C<sub>1</sub>-C<sub>4</sub> alkyl; (11) R<sup>e</sup>C(O)- wherein R<sup>e</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>1</sub>-C<sub>4</sub> alkoxy; or (12) SO<sub>2</sub>NRCR<sup>d</sup> wherein R<sup>c</sup> and R<sup>d</sup> are as defined, with the proviso that R<sup>7</sup> is not attached to the 6-position comprising

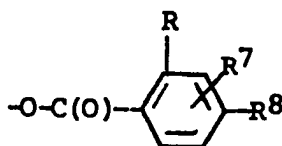
(a) reacting a dione of the formula



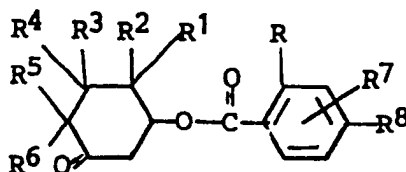
5 wherein R<sup>1</sup> through R<sup>6</sup> are as defined with a substituted benzoyl reactant of the formula



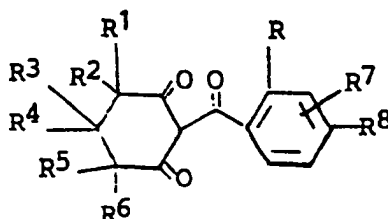
wherein R, R<sup>7</sup> and R<sup>8</sup> are as defined and X is halogen, C<sub>1</sub>-C<sub>4</sub> alkyl-C(O)-O-, C<sub>1</sub>-C<sub>4</sub> alkoxy-C(O)-O- or



wherein R, R<sup>7</sup> and R<sup>8</sup> in this portion of the molecule are identical with those in the reactant shown above with at least a mole of a moderate base to form an enol ester of the formula



wherein R through R<sup>8</sup> are as defined and in step (2) reacting a mole of the enol ester intermediate with 1 to 4 moles of a moderate base, and from 0.01 mole to about 0.5 mole or higher of a cyanide source to form a compound of the formula



wherein R<sup>1</sup> through R<sup>8</sup> are as defined above.

38. The process of Claim 37 wherein X is halogen, the moderate base is tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, pyridine, alkali metal carbonate or alkali metal phosphate and the cyanide source alkali metal cyanide, cyanohydrins of methyl C<sub>1</sub>-C<sub>4</sub> alkyl ketones, cyanohydrins of benzaldehyde or C<sub>2</sub>-C<sub>5</sub> aliphatic aldehydes; cyanohydrins, zinc cyanide; tri(lower alkyl) silyl cyanides or hydrogen cyanide.

39. The process of Claim 38 wherein X is chlorine, the moderate base is tri-C<sub>1</sub>-C<sub>6</sub> alkylamine, pyridine, sodium carbonate or sodium phosphate and the cyanide source is potassium cyanide, acetone cyanohydrin or hydrogen cyanide.



European Patent  
Office

# EUROPEAN SEARCH REPORT

0186120  
Application number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 85116167.9
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
P,A	<u>EP - A1 - 0 137 963</u> (STAUFFER CHEMICAL)  * Claims 1,20 * --	1,20, 21,23	C 07 C 49/792 C 07 C 121/64 C 07 C 147/06 C 07 C 149/32 A 01 N 35/06
P,A	<u>EP - A2 - 0 135 191</u> (STAUFFER CHEMICAL)  * Claims 1,8 * --	1,20, 21,23	
D,A	<u>EP - A2 - 0 090 262</u> (STAUFFER CHEMICAL)  * Claims 1,14 * --	1,20, 21,23	
A	<u>EP - A1 - 0 017 195</u> (EISAI CO.)  * Claims 1,19; examples 82,83 * ----	1,37	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 49/00 C 07 C 121/00 C 07 C 147/00 C 07 C 149/00
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 06-03-1986	Examiner REIF
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	